

1 **Attribution of recovery in lower-stratospheric ozone**

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12

13 **Abstract**

14

15 **Multiple satellite and ground-based observations provide consistent evidence that the**  
16 **thickness of Earth's protective ozone layer has stopped declining since 1997, close to the**  
17 **time of peak stratospheric halogen loading. Regression analyses with Effective Equivalent**  
18 **Stratospheric Chlorine (EESC) in conjunction with further analyses using more**  
19 **sophisticated photochemical model calculations constrained by satellite data demonstrate**  
20 **that the cessation of ozone depletion between 18-25 km altitude is consistent with a**  
21 **leveling off of stratospheric abundances of chlorine and bromine, due to the Montreal**  
22 **Protocol and its amendments. However, ozone increases in the lowest part of the**  
23 **stratosphere, from the tropopause to 18 km, account for about half of the improvement in**  
24 **total column ozone during the past 9 years at northern hemisphere mid-latitudes. The**  
25 **increase in ozone for altitudes below 18 km is most likely driven by changes in transport,**  
26 **rather than driven by declining chlorine and bromine. Even with this evidence that the**  
27 **Montreal Protocol and its amendments are having the desired, positive effect on ozone**  
28 **above 18 km, total column ozone is recovering faster than expected due to the apparent**  
29 **transport driven changes at lower altitudes. Accurate prediction of future levels of**  
30 **stratospheric ozone will require comprehensive understanding of the factors that drive**  
31 **temporal changes at various altitudes, and partitioning of the recent transport-driven**  
32 **increases between natural variability and changes in atmospheric structure perhaps**  
33 **related to anthropogenic climate change.**

1 **1. Introduction**

2 Atmospheric ozone, which protects life on Earth's surface from damaging solar ultraviolet  
3 radiation, exists mostly (~90% of the total column) in the stratosphere. The decrease in  
4 stratospheric ozone and the character of its expected recovery have been the subject of intense  
5 research [WMO, 2003]. Recently reported evidence for the first stage of recovery (i.e., a  
6 slowdown in the ozone depletion rate) in the upper stratosphere at 35-45 km [Newchurch *et al.*,  
7 2003b; Reinsel *et al.*, 2002] has confirmed our understanding of ozone chemistry and the positive  
8 effect of the Montreal Protocol and its amendments, which have led to a decline in stratospheric  
9 halogen (chlorine and bromine) loading. However, the largest fraction of the ozone column  
10 resides in the lower stratosphere, between approximately 10 and 25 km altitude [WMO, 1999].  
11 The abundance of ozone in the lower stratosphere is the essential metric for confirming the health  
12 of the ozone layer.

13 Stratospheric ozone is continually produced by photolysis of molecular oxygen and is  
14 removed locally by both transport and chemical processes. In the upper stratosphere, transport  
15 plays a minor role and there is a direct, almost linear anti-correlation between the abundances of  
16 ozone and chlorine [e.g., figure 6-21, WMO, 1999]. The majority of stratospheric chlorine is  
17 supplied by industrial pollutants, such as CFCs (chlorofluorocarbons). Ozone in the lower  
18 stratosphere is sensitive to re-distribution by atmospheric transport, the abundance of volcanic  
19 aerosols, and a complex set of non-linear chemical interactions involving anthropogenic chlorine  
20 and bromine [chapter 7, WMO, 1999; chapter 4, WMO, 2003]. A number of recent studies, based  
21 on examination of time series of total column ozone, have noted a turnaround in the recent  
22 downward trend [Reinsel *et al.*, 2005; Steinbrecht *et al.*, 2005; Hadjinicolaou *et al.*, 2005] that  
23 may be evidence for the beginning of an ozone recovery due to declining halogen loading  
24 [Reinsel *et al.*, 2005]. However, Hadjinicolaou *et al.* [2005] attribute the recent turnaround in total  
25 column ozone to effects of transport. Here, we examine changes in total column ozone as well as  
26 partial ozone columns, in specific altitude regions, to better ascertain effects of halogen chemistry  
27 (i.e., chlorine and bromine) and transport forcings on recent changes in stratospheric ozone. Our  
28 focus is on changes in ozone that have occurred outside the polar regions; our analyses are

1 restricted to regions equatorward of 60° latitude. The long-term evolution of polar ozone is  
2 sensitive to changes in stratospheric temperature that may be linked to climate change, as well  
3 as evolving levels of chlorine and bromine, and is the subject of many other studies [Austin *et al.*,  
4 2002; Austin, 2003; Huck *et al.*, 2005; Newman *et al.*, 2004; Rex *et al.*, 2004; Shindell *et al.*,  
5 1998; Solomon *et al.*, 2005; Yang *et al.*, 2005]. However, the influence of polar ozone loss on the  
6 extra-polar ozone time series [Reinsel *et al.*, 2005; Weatherhead and Andersen, 2005] is  
7 considered in this study.

8 Recently, the International Ozone Commission <http://ioc.atmos.uiuc.edu/documents/Statement-QOS2004.pdf> defined the first stage of ozone recovery as a 'statistically significant  
9 slowing of the downward trend'. Our study focuses on empirical evidence for this first stage of  
10 ozone recovery that is evident from several independent measurement systems and networks  
11 covering large portions of the global atmosphere during the past 25 years. These independent  
12 observing techniques show a consistent slowdown in the loss rates in total ozone columns,  
13 stratospheric ozone columns, and ozone columns between 18-25 km (near the ozone-layer  
14 maximum). Our study focuses on the attribution of changes in ozone at mid-latitudes by  
15 examining the role of chemistry and transport forcings on observed changes in partial column  
16 ozone, for layers between 18-25 km and the tropopause to 18 km. The significance of these  
17 changes is quantified by a cumulative sum of residuals analysis [Newchurch *et al.*, 2003b;  
18 Reinsel, 2002]. A photochemical model, constrained by satellite observations of tracers of  
19 atmospheric transport, volcanic aerosol loading, and numerous other chemical measurements, is  
20 also used to quantify the expected increases in ozone due to declining levels of stratospheric  
21 chlorine and bromine that have resulted from the Montreal Protocol and its amendments.

23

## 24 **2. Data**

25 The most comprehensive representation of changes in the global stratospheric ozone  
26 layer is based on the consistent results of three independent satellite instruments and two  
27 independent ground-based observing networks. We analyze the TOMS/SBUV satellite  
28 measurements to characterize total-column ozone changes from 60°S to 60°N latitudes. From the

1 well-calibrated ground-based networks, we use 36 Dobson/Brewer stations between 30°S-60°N  
2 to corroborate the satellite total-column ozone results. We use both SAGE and HALOE satellite  
3 measurements to characterize the global stratosphere above 18 km, between 60°S and 60°N.  
4 These ozone data are area-weighted to compute near-global mean values. Because most of the  
5 total-column ozone amount resides in the stratosphere and because the global mixing time is  
6 significantly less than the decadal time frame important here, we expect to see broadly consistent  
7 recovery signatures from all of these independent measurements.

8 The Stratospheric Aerosol and Gas Experiment I and II (SAGE I/II) instruments comprise  
9 the longest (1979 to August 22, 2005, but with a discontinuity between November, 1981 and  
10 October, 1984) and most widely analyzed source of global stratospheric ozone measurements  
11 [Cunnold et al., 2000; Newchurch et al., 2000; WMO, 2003]. The complete version-6.2 data set  
12 and details of the retrieval algorithm are available through <http://www-sage2.larc.nasa.gov>.

13 The version-19 Halogen Occultation Experiment (HALOE) data for 1991 to November 21,  
14 2005 comprise a shorter, but equally accurate record of stratospheric ozone amounts, in addition  
15 to measurements of other trace gases critical to partitioning the chemical and dynamical causes  
16 of the improving ozone layer [Russell III et al., 1993]. The HALOE data are available at  
17 <http://haloedata.larc.nasa.gov>. Both SAGE and HALOE measurements have been extensively  
18 validated [Ackerman et al., 1989; Attmannspacher et al., 1989; Cunnold et al., 1989; Cunnold et  
19 al., 1996; Gordley et al., 1996; Hervig et al., 1996; Newchurch et al., 1995; Oberbeck et al., 1989;  
20 Russell III et al., 1996a,b; Wang et al., 2002] and are widely accepted by the atmospheric  
21 community for studies of ozone trends [Harris et al., 1998; WMO, 1994; WMO, 2003].

22 We also analyze global total ozone data from the merged Total Ozone Mapping  
23 Spectrometer (TOMS)/SBUV data (Merged Ozone Data, herein after referred to as the MOD),  
24 which provide nearly continuous global coverage since 1979 [McPeters et al., 1996; McPeters  
25 and Labow, 1996; Reinsel et al., 1994; Stolarski et al., 1991] (details at  
26 [http://code916.gsfc.nasa.gov/Data\\_services/merged/](http://code916.gsfc.nasa.gov/Data_services/merged/)). Total ozone measurements observed from  
27 the ground-based Dobson [Dobson, 1931; Dobson, 1968; Dobson and Harrison, 1926; Dobson et  
28 al., 1928; Komhyr et al., 1989; Lloyd et al., 1999; Newchurch et al., 2000; Staehelin et al., 1998;

1 Staehelin et al., 1995; WMO, 2003] and Brewer [Bais et al., 1996; Hoegger et al., 1992; Kerr et  
2 al., 1988; Lloyd et al., 1999; McElroy and Kerr, 1995; Slusser et al., 1999; Staehelin et al., 1995]  
3 spectrophotometers are obtained from the World Ozone and Ultraviolet Radiation Data Centre  
4 (WOUDC) (<http://www.msc-smc.ec.gc.ca/woudc>). These data are mostly selected based on table  
5 4-4 of WMO [1999]: 26 Dobson/Brewer stations between 30-60°N (Kagoshima, Quetta, Sapporo,  
6 Tateno, Bismarck, Caribou, Edmonton, Arosa, Camborne, Haute Provence, Potsdam, Uccle,  
7 Vigna Di Valle, Toronto, Boulder, Belsk, Goose Bay, Churchill, Lisbon, Hradec Kralove,  
8 Hohenpeissenberg, Nashville, Wallops Island, Cairo, Sestola, and Xianghe) and 10  
9 Dobson/Brewer stations between 30°S-30°N (Kodaikanal, New Delhi, Mauna Loa, Varanasi,  
10 Naha, Samoa, Cachoeira Paulista, Kunming, Singapore, and Natal). The selected data follow the  
11 corrections recommended by WMO [1999, section 4.2]. Balloon-borne ozonesonde  
12 measurements [Newchurch et al., 2003a; Oltmans et al., 1998; Oltmans et al., 1996] from 11  
13 stations between 30-60°N (Kagoshima, Sapporo, Tateno, Edmonton, Uccle, Boulder, Goose Bay,  
14 Churchill, Hohenpeissenberg, Wallops Island, and Payerne), obtained from the WOUDC, are  
15 used to derive reliable long-term trends of ozone from the surface to 27 km [page 4.14, WMO,  
16 1999]. Ozone columns are calculated both in the lower stratosphere between the tropopause and  
17 18 km (TP-18 km) and in the middle stratosphere (18-25 km near the maximum layer in ozone  
18 concentration).

19

20 **3. Statistical model**

21 We employ a stepwise linear regression model to remove solar and Quasi Biennial  
22 Oscillation (QBO)-related signals from the ozone time series [Newchurch et al., 2000; Newchurch  
23 et al., 2003b]. Variations in solar ultraviolet radiation due to the 11-year cycle of solar sunspots,  
24 and changes in the direction of stratospheric winds in the tropics that vary on a roughly 2.5-year  
25 period, are known to affect measured time series of stratospheric and total column ozone.  
26 Because our emphasis is on the identification of variations in ozone due to changes in halogen  
27 loading, a statistical model is used to account for, and remove, the effects of these processes on  
28 the measured time series. Seasonal effects and the mean abundance of ozone over the time

1 period are also removed, providing a residual time series that is examined for evidence of ozone-  
2 layer recovery.

3 The linear regression model is well accepted by the atmospheric sciences community  
4 [Harris et al., 1998] and is represented by

5

6  $[O_3]_t = \mu + \omega t + [\text{Seasonal terms}] + [\text{QBO periodic terms}] + \gamma [F10.7]_t + U_t$  (1)

7

8 where  $\mu$  is the mean level,  $\omega$  is a linear trend coefficient, and the seasonal terms represent the  
9 12-, 6-, 4-, and/or 3-months cosine terms each with a time lag to obtain the best estimate of its  
10 coefficient. The QBO periodic terms consist of an ensemble of cosines with time lags to represent  
11 the QBO signal with periods between 3 and 30 months excluding 12-, 6-, 4-, and/or 3-months  
12 terms, which are included in the seasonal coefficients.  $[F10.7]_t$  is the F10.7-cm radio flux density,  
13 which is used to provide a proxy for variations in solar UV irradiance.  $\gamma$  is a solar signal  
14 regression coefficient.  $U_t$  is the autocorrelated error term, representing a first-order  
15 autoregressive process ( $U_t = a_1 U_{t-1} + \varepsilon_t$ ).

16 Based on surface measurements of ozone depleting substances and the time lag ( $\sim 3$   
17 years) involved in their rising to the altitude of the stratospheric ozone layer at mid-latitudes, we  
18 choose the start of 1997 as the time to test for an inflection in the ozone time series [Montzka et  
19 al., 1999; WMO, 2003]. The Effective Equivalent Stratospheric Chlorine (EESC), a combined  
20 measure of lower stratospheric abundances of inorganic chlorine and bromine, peaked in mid-  
21 1996 [figure 1-23, WMO, 2003]. The effect of the autoregressive coefficient on the subsequent  
22 uncertainty calculation is described in the appendix. Details of the treatment of exogenous  
23 variables appear in Newchurch et al. [2003b].

24 An aerosol term is not included in the regression. Highly-elevated aerosol loading  
25 following major volcanic eruptions interferes with the space-borne measurement of lower  
26 stratospheric ozone [Cunnold et al., 2000]. Of course, ozone depletion results from changes in  
27 heterogeneous chemistry associated with enhanced aerosol loading following major volcanic  
28 eruptions [e.g., Dessler et al., 1993; Fahey et al., 1993; Wennberg et al., 1994; Kinnison et al.,

1 1994]. Changes in stratospheric heating associated with volcanic aerosols lead to additional  
2 short-term variations in ozone [e.g., *Kinne et al.*, 1992; *Kinnison et al.*, 1994; *Robock*, 2000]. We  
3 have omitted data collected up to 30 months following the eruption of Mt. Pinatubo from the  
4 SAGE and HALOE time series due to the aerosol influence on space-based ozone [*Cunnold et*  
5 *al.*, 2000] and also because our analysis is focused on long term changes in ozone for  
6 stratospheric aerosol conditions close to background. We also omit the merged TOMS/SBUV  
7 data, Dobson/Brewer total ozone, and ozonesonde ozone records for 1991.5-1994.0 to be  
8 consistent with the statistical treatment of the SAGE and HALOE satellite records and because  
9 our study is focused on near background aerosol conditions. The omission of data for time  
10 periods perturbed by enhanced volcanic aerosols is a common practice in regression based  
11 analyses of ozone time series: e.g., *Reinsel et al.* [2005] omit data influenced by Pinatubo, as  
12 explained in paragraph 10 of their paper. Here, we show data collected during the Pinatubo time  
13 period, plotted as open circles, but we do not include these data in our statistical analyses.

14

#### 15 **4. Photochemical Model**

16 The attribution of changes in ozone is based independently on EESC regression and on  
17 more sophisticated photochemical model calculations constrained by observations of tracers of  
18 dynamical motion and stratospheric aerosol. The EESC time series is based on measurements of  
19 tropospheric total organic chlorine ( $CCl_y$ ) and bromine ( $CBry$ ). It is lagged relative to the surface  
20 by three years [pages 1.32 and 11.15, *WMO*, 1999 and page 1.19, *WMO*, 2003]. The efficiency of  
21 ozone loss due to bromine relative to chlorine, which is based on photochemical model  
22 simulations, is used to arrive at a single time series to represent the aggregate effect of halogens  
23 on ozone [alpha factor, page 1.69, *WMO*, 2003].

24 Many studies which have focused on attribution of ozone changes have used EESC to  
25 represent the effects of halogens on ozone [e.g., *Newman et al.*, 2004; *Huck et al.*, 2005; *Yang et*  
26 *al.*, 2005]. However, EESC is a simplistic representation of the influence of chlorine and bromine  
27 on ozone. Not all stratospheric air is three years old, as assumed in the formulation of EESC.  
28 Also, the relative influence of chlorine and bromine on ozone loss varies as a function of altitude,

1 latitude, season, and aerosol loading. The formulation of EESC assumes a single relative-  
2 influence factor that has the same value at all latitudes and altitudes. However, the contribution of  
3 halogens to ozone loss varies as a function of aerosol loading [e.g., *Dessler et al.*, 1993; *Fahey*  
4 *et al.*, 1993; *Kinnison et al.*, 1994] and as a function of the abundance of HO<sub>x</sub> (hydrogen oxide)  
5 and NO<sub>x</sub> (nitrogen oxide) radicals. In turn, HO<sub>x</sub> and NO<sub>x</sub> variations are also driven by changes in  
6 H<sub>2</sub>O, CH<sub>4</sub>, and temperature [e.g., *Salawitch et al.*, 1994; *Wennberg et al.*, 1994]. Also, bromine  
7 has a larger relative influence on ozone loss near the tropopause than at higher altitudes [e.g.,  
8 *Salawitch et al.*, 2005].

9 We have used a photochemical model, constrained by satellite measurements of water  
10 vapor (H<sub>2</sub>O), ozone (O<sub>3</sub>), methane (CH<sub>4</sub>), and sulfate aerosols, to compute 24-hour-average  
11 radical abundances (e.g., ClO, BrO, OH, HO<sub>2</sub>, NO, and NO<sub>2</sub>) for all altitudes, latitudes, and time  
12 periods under consideration. The fractional contribution of halogens to total ozone loss found  
13 from these calculated radical fields, termed LOSS<sub>MODEL</sub>, is also used as a regression variable in  
14 the analysis discussed in Section 5. The quantity LOSS<sub>MODEL</sub>, described more fully below, can be  
15 thought of as a more sophisticated version of EESC.

16 Here, we describe the procedure used to estimate LOSS<sub>MODEL</sub>. We estimate the fraction  
17 of ozone loss due to halogens for each month of the ozone time series, at 1-km intervals between  
18 18 and 25 km, for latitudes of 55°N, 45°N, 35°N, 5°N, 5°S, 35°S, 45°S and 55°S. The model is  
19 constrained by zonal, monthly mean values of H<sub>2</sub>O, CH<sub>4</sub>, and O<sub>3</sub>, all observed by HALOE  
20 [Russell III et al., 1993]. Prior to the launch of HALOE, SAGE II measurements of O<sub>3</sub> are used.  
21 Aerosol surface area is obtained from SAGE I and SAGE II observations [Thomason and Poole,  
22 1997]. First, N<sub>2</sub>O is calculated from HALOE zonal, monthly mean CH<sub>4</sub> using the formula of  
23 Michelsen et al. [1998]. Different relations are used for tropical and mid-latitude regions. The  
24 shapes of these relations are related to the relative lifetime of each species in the tropics and  
25 mid-latitude regions, respectively. The ATMOS relations that covered several weeks of  
26 observations at many latitudes have been shown to agree well with in situ [e.g., Herman et al.,  
27 1998] and aircraft [e.g., Chang et al., 1996a] observations of these relations, obtained at other  
28 time periods. We allowed for growth in N<sub>2</sub>O over time of 0.315% per year, relative to 1994.875

1 (the time of the *Michelsen et al.* [1998] ATMOS observations), which is obtained from data in  
2 table 1-12 of *WMO* [1999]. We allowed for growth of CH<sub>4</sub> of 5.0 ppbv/year from 1979 until 2000  
3 and of 2 ppbv/year from 2000 onward, again relative to 1994.875. These values are obtained  
4 from section 1.7.2 of *WMO* [2003]. These small growth rates were implemented so that the  
5 formula of *Michelsen et al.* [1998] could be incorporated more realistically into the model, which is  
6 driven ultimately by HALOE CH<sub>4</sub>: e.g., prior to input to the *Michelsen et al.* formula, HALOE CH<sub>4</sub>  
7 was converted to its equivalent value for 1994.875; a value of N<sub>2</sub>O was found using the  
8 appropriate relation, based on latitude zone; then, the computed value of N<sub>2</sub>O was scaled to the  
9 time of the actual CH<sub>4</sub> observation. The growth rates for N<sub>2</sub>O and CH<sub>4</sub> are a minor part of the  
10 overall analysis and have no bearing on the final results.

11 Inorganic chlorine (Cl<sub>y</sub>) is estimated based on the formulation derived from aircraft  
12 measurements of organic chlorine compounds that is described by *Woodbridge et al.* [1995]. As  
13 noted above, N<sub>2</sub>O is estimated from HALOE CH<sub>4</sub>, using the formula from *Michelsen et al.* [1998],  
14 allowing for the small temporal growth in both N<sub>2</sub>O and CH<sub>4</sub> described above. For the estimate of  
15 Cl<sub>y</sub>, the following relation with N<sub>2</sub>O was used:

$$[Cl_y] = 3.53876 - 2.57709 \times 10^{-3} [N_2O] - 1.91693 \times 10^{-5} [N_2O]^2 - 2.40584 \times 10^{-8} [N_2O]^3 \quad (2)$$

16 where [Cl<sub>y</sub>] and [N<sub>2</sub>O] are in ppbv. This relation is based on in situ measurements of a complete  
17 set of halocarbons obtained during the SOLVE campaign [*Schauffler et al.*, 2003]. All other  
18 aspects of the computation of Cl<sub>y</sub> are based on the method described by *Woodbridge et al.*  
19 [1995], which allows for Cl<sub>y</sub> to be computed for earlier time periods by adjusting the value of total  
20 chlorine in the troposphere [equation 11 of *Woodbridge et al.*, 1995].

21 Inorganic bromine (Br<sub>y</sub>) is estimated based on a relation derived from aircraft  
22 measurements of the bromocarbon source gases and nitrous oxide (N<sub>2</sub>O) [*Wamsley et al.*, 1998].  
23 For the estimate of Br<sub>y</sub>, a correlation with CFC-11 is used, because the primary bromine source  
24 gas, CH<sub>3</sub>Br, has a stratospheric lifetime somewhat similar to lifetime of CFC-11 [e.g., plate 1 of  
25 *Wamsley et al.*, 1998]. Equations 15 and 16 of *Wamsley et al.* [1998] are used to estimate CFC-  
26 11 from N<sub>2</sub>O, based on whether data was obtained in the tropics or extratropics, respectively.

1 We allow for variations in the age of air in the calculation of  $\text{Cl}_y$  and  $\text{Br}_y$ , as outlined by  
2 *Woodbridge et al.* [1995] and *Wamsley et al.* [1998], using the relation between age and  $\text{N}_2\text{O}$   
3 given in figure 2.12 of *Park et al.* [1999]. This relation between age of air and  $\text{N}_2\text{O}$  is very similar  
4 to an independent determination reported by *Engel et al.* [2002]. Finally, the temporal evolution of  
5  $\text{CCl}_y$  and  $\text{CBr}_y$ , which appear as factors in the formula for  $\text{Cl}_y$  and  $\text{Br}_y$  [e.g., *Woodbridge et al.*,  
6 1995; *Wamsley et al.*, 1998], is based on the WMO 2003 Ab baseline scenario [e.g., table 1-16,  
7 WMO, 2003]. This method for estimating  $\text{Cl}_y$  and  $\text{Br}_y$  from tracers has been used in many  
8 empirical studies of balloon and aircraft data [e.g., *Chang et al.*, 1996a; *Salawitch et al.*, 1994;  
9 *Salawitch et al.*, 2005 and references therein] and is a common tool for estimating time series of  
10 halogens [e.g., *Engel et al.*, 2002].

11 A second set of calculations was conducted for the tropical region. The use of HALOE  
12  $\text{CH}_4$  to prescribe model  $\text{Cl}_y$  and  $\text{NO}_y$  for 18 to 25 km in the tropics is a challenge, because  
13 measured  $\text{CH}_4$  lies close to its tropopause value. Hence, small uncertainties in measured  $\text{CH}_4$   
14 can lead to large relative errors in estimated  $\text{Cl}_y$  and  $\text{NO}_y$ . For this second set of calculations,  
15 model  $\text{HCl}$  and  $\text{NO}_x$  was constrained to match the zonal, monthly mean HALOE observations of  
16 these quantities by adjusted model  $\text{Cl}_y$  and  $\text{NO}_y$  to match the data. Both sunrise and sunset  
17 observations were used, with the model matching the appropriate time of observation. Model  $\text{Br}_y$   
18 was scaled to preserve the  $\text{Cl}_y$  to  $\text{Br}_y$  ratio for the particular time of observation. Monthly mean  
19 values of  $\text{Cl}_y$ ,  $\text{Br}_y$ , and  $\text{NO}_y$ , normalized to year 1993.0, were computed for each latitude region  
20 over the UARS time period. These monthly mean values were propagated backwards in time to  
21 cover the time period between 1979 and the first data from HALOE, using the known temporal  
22 changes in organic chlorine, organic bromine, and  $\text{N}_2\text{O}$  (e.g., WMO 2002 Ab scenario for  $\text{CCl}_y$   
23 and  $\text{CBr}_y$ , augmented by constant values of  $\text{CH}_2\text{Br}_2$  and  $\text{CH}_2\text{BrCl}$  for  $\text{Br}_y$ ;  $\text{NO}_y$  growth of 0.315%  
24 per year, based on the  $\text{N}_2\text{O}$  growth described above).

25 Estimates of  $\text{NO}_y$  are based on its relation with  $\text{N}_2\text{O}$ . For values of  $\text{N}_2\text{O} < 150$  ppb, we  
26 use the formula of *Rinsland et al.* [1999]. For  $\text{N}_2\text{O} > 150$  ppb, the relation of *Popp et al.* [2001] is  
27 used. The *Rinsland et al.* [1999] relation is based on measurements from ATMOS; the *Popp et al.*  
28 [2001] relation is based on data from aircraft and balloons. The relation between  $\text{NO}_y$  and  $\text{N}_2\text{O}$  is

1 robust, displaying small variations outside the polar regions [e.g., *Sen et al.*, 1998; *Keim et al.*,  
2 1997]. Indeed, various coupled climate and chemistry models, as well as 2D and 3D models,  
3 display much larger variations in the  $\text{NO}_y$  vs  $\text{N}_2\text{O}$  relation (compared to either other models, or to  
4 data) than is commonly seen in measurements from different instruments [e.g., *Chang et al.*,  
5 1996b; *Park et al.*, 1999]. The good agreement between measured and modeled  $\text{NO}_x$ , illustrated  
6 in Figure 1, again provides confidence in the fidelity of this approach. As for  $\text{HCl}$ , excellent  
7 agreement is found for altitudes above 19 km. At 19 km and lower altitudes, small measurement  
8 uncertainties in  $\text{CH}_4$  have a large affect on the model results, because the tracer-tracer relations  
9 are approaching tropopause values that lie close to zero. Similar comparisons between measured  
10 and modeled  $\text{NO}_x$  are found for other latitudes (not shown).

11 The model is constrained by observations of  $\text{CH}_4$  and  $\text{H}_2\text{O}$ , which are important for  
12 calculating  $\text{HO}_x$  radicals. For the UARS time period, zonal, monthly mean observations from  
13 HALOE are used. For the pre-UARS time period, we propagated back in time the monthly mean  
14 value of  $\text{H}_2\text{O}$ , for the specific latitude and altitude point, derived from HALOE measurements and  
15 assuming zero trend for  $\text{H}_2\text{O}$ . A similar treatment is used for  $\text{CH}_4$ , except we allow for the small  
16 temporal trend noted above. In other words, for all Januaries prior to the launch of UARS, the  
17 same value of  $\text{H}_2\text{O}$  is used for the model grid point in question (function of altitude and latitude),  
18 which is derived from a mean of all model grid points (at the same altitude and latitude) for times  
19 when data are available. The trends in  $\text{H}_2\text{O}$  are uncertain, particularly prior to the launch of UARS  
20 [SPARC, 2000]. However, the scientific results of this paper, the attribution of changes in ozone  
21 to the leveling off of  $\text{Cl}_y$  and  $\text{Br}_y$ , are insensitive to any reasonable assumption regarding  $d\text{H}_2\text{O}/dt$   
22 over the pre-UARS time period. The reason for this insensitivity is that the abundance of  $\text{HO}_x$   
23 varies in proportion to changes in the square root of the concentration of  $\text{H}_2\text{O}$ . Finally, there are  
24 occasional gaps in monthly, zonal mean HALOE and SAGE II data due to the sampling of the  
25 respective instruments. For these occasions, which are rare in the overall analysis, values of  
26  $\text{LOSS}_{\text{MODEL}}$  are not computed, and this information is treated as “not available” in the CUSUM  
27 analysis of these model results.

1 Figure 1 compares modeled and measured HCl (sunrise and sunset) and NO<sub>x</sub> (sunset) at  
2 20 and 25 km, for three latitude regions. The good agreement between modeled and measured  
3 HCl and NO<sub>x</sub> demonstrates the reliability of the approach. A model calculation for the tropics,  
4 based on specification of Cl<sub>y</sub> and NO<sub>y</sub> from measured CH<sub>4</sub>, tends to simulate HCl and NO<sub>x</sub>  
5 reasonably well at 25 km (not shown). However, this model overestimates both HCl and NO<sub>x</sub> at  
6 20 km, because the HALOE CH<sub>4</sub> time series lies close to tropopause values of CH<sub>4</sub>, which  
7 introduces uncertainties in estimates of Cl<sub>y</sub> and NO<sub>y</sub> based on this “tracer-tracer” approach.  
8 Hence, for the tropics, we show here and use in our CUSUM analysis the model calculation  
9 constrained to match HALOE HCl and NO<sub>x</sub>. The resulting CUSUMs of LOSS<sub>MODEL</sub> for both of  
10 these calculations in the tropics are remarkably similar, however, as discussed in Section 5.

11 Finally, since we are using the formula of *Wamsley et al.* [1998] to derive Br<sub>y</sub>, the derived  
12 values are ~2.4 ppt higher than values that would be derived from consideration of supply of  
13 bromine from only CH<sub>3</sub>Br and halons. Here, we assume CH<sub>2</sub>Br<sub>2</sub> and CH<sub>2</sub>BrCl are constant over  
14 time. The values of Br<sub>y</sub> in this model are smaller than values inferred from some measurements  
15 of BrO [e.g., *Salawitch et al.*, 2005], possibly due to an important role for stratospheric supply of  
16 bromine from biogenic bromocarbons. However, the role of biogenic bromocarbons on  
17 stratospheric Br<sub>y</sub> is a subject of active research [e.g., *Salawitch*, 2006]: retrievals of BrO from  
18 SCIAMACHY by one group suggest a modest role for this source [*Sinnhuber et al.*, 2005], in line  
19 with the approach used here, whereas retrievals from another group suggest a much larger role  
20 for biogenic bromine [*Sioris et al.*, 2006]. An attempt to model the role of biogenic bromocarbons  
21 is beyond the scope of this paper, although in Section 5 we comment about the possible affect of  
22 these compounds on the attribution of ozone changes in the lowermost stratosphere.

23 Our approach allows us to calculate how ozone loss by halogens has evolved over time  
24 in response to changes in chlorine, bromine, water, methane, HO<sub>x</sub>, NO<sub>x</sub>, and sulfate aerosol  
25 loading as well as variations in atmospheric transport. Changes in transport are reflected in  
26 changes in CH<sub>4</sub>, which controls the input fields of NO<sub>y</sub>, Cl<sub>y</sub>, and Br<sub>y</sub>. This model has been shown  
27 to provide accurate simulations of hydrogen, nitrogen, and chlorine radical species under a  
28 variety of aerosol loading, seasonal, and latitudinal conditions [*Osterman et al.*, 1997; *Salawitch*,

1 2002; *Sen et al.*, 1999; *Sen et al.*, 1998]. Model results are integrated from 18 to 25 km, weighted  
2 by the concentration of ozone at each altitude. Similar results are found if we were to use equal  
3 weights for each altitude (this weighting is almost identical to a non-weighted average because  
4 the ozone contents of each 1-km layer are almost all equal). The resulting time series is referred  
5 to as  $\text{LOSS}_{\text{MODEL}}$ . Plots of  $\text{LOSS}_{\text{MODEL}}$  for 7 latitude bands centered between 60°S and 60°N are  
6 shown in Figure 2. The calculated increase in ozone loss by halogens between 1979 and 2005 is  
7 consistent with the overall rise in stratospheric chlorine and bromine loading (top panel, Figure 2).  
8 However, ozone loss by halogens peaked near 1992, which is expected based on known  
9 photochemistry in the presence of highly elevated abundances of stratospheric aerosol following  
10 the eruption of Mt. Pinatubo [*Dessler et al.*, 1993; *Fahey et al.*, 1993]. Figure 2 shows results for  
11  $\text{LOSS}_{\text{MODEL}}$  in the tropics (10°S to 10°N) for the model constrained by measured  $\text{HCl}$  and  $\text{NO}_x$ ,  
12 which is a more accurate empirical approach for this region of the atmosphere, where the tracer-  
13 tracer relation approach introduces some uncertainty. Interestingly, however, nearly identical  
14 results for  $\text{LOSS}_{\text{MODEL}}$  are found for the tropics using the tracer-tracer approach. Ozone loss in  
15 the tropics is found from a balance between halogen and  $\text{HO}_x$  photochemistry and decreases in  
16  $\text{H}_2\text{O}$  and  $\text{CH}_4$  measured by HALOE since ~2002 result in the points for  $\text{LOSS}_{\text{MODEL}}$ , for the past 4  
17 years, lying above the blue curve (EESC fit to  $\text{LOSS}_{\text{MODEL}}$ ) by comparable amounts for both  
18 simulations.

19 An outstanding scientific issue, which is not addressed in our study, is that even though  
20 the effect of enhanced chemical loss of ozone due to Pinatubo aerosols is readily apparent from  
21 various ozone datasets in the Northern Hemisphere, this same effect is not apparent from  
22 measurements in ozone obtained in the Southern Hemisphere [section 4.6.6, *WMO*, 2003]. The  
23 reason for this disparity is a subject of active research and is especially puzzling given the large,  
24 Pinatubo induced decline in column  $\text{NO}_2$  observed at Lauder, New Zealand [e.g., figure 4-21,  
25 *WMO*, 2003]. We avoid this confounding issue by omitting in our analysis data collected during  
26 times of highly perturbed aerosol loading.

27 Two time series are used independently for the attribution of ozone loss by halogens:  
28 values of EESC (Figure 2) from *WMO* [2003] Ab baseline scenario and values of  $\text{Loss}_{\text{MODEL}}$ . The

1 EESC time series allows observed changes in  $O_3$  to be related to well-established variations in  
2 the abundance of stratospheric halogens. The  $Loss_{MODEL}$  time series is a refinement to the EESC-  
3 based estimate, allowing the changes in  $O_3$  to be related to the time evolution of ozone loss by  
4 halogens accounting for "age of air" as well as observed changes in  $CH_4$ ,  $H_2O$ , aerosol loading,  
5  $NO_x$  and  $HO_x$  radicals, in addition to variations in  $Cl_y$  and  $Br_y$ .

6

## 7 5. Changes in ozone trends

8 The three left panels in Figure 3 show the residual ozone time series from SAGE and  
9 HALOE (top), Dobson/Brewer spectrophotometers (middle), and the merged TOMS/SBUV  
10 satellite instruments (bottom) that remain after the mean, seasonal, QBO, and solar terms have  
11 been removed, as described in Equation (1). The excellent agreement between the SAGE and  
12 HALOE measurements of the temporal evolution of stratospheric ozone is apparent in the top left  
13 panel. Likewise, the linear trends from 1979.0 to the end of 1996 (=1997.0) from SAGE ( $-2.3 \pm$   
14  $0.2 \text{ \%/decade}$  with  $2\sigma$  uncertainty), Dobson/Brewer ( $-2.1 \pm 0.5 \text{ \%/decade}$ ), and the MOD ( $-1.6 \pm$   
15  $0.3 \text{ \%/decade}$ ) are consistent over a broad portion of Earth's atmosphere.

16 We calculate the cumulative departure of the measured ozone from the 1979-1996 trend  
17 line (solid black line) extended forward to the time period 1997 to 2005, using the cumulative sum  
18 (CUSUM) of residuals technique [Newchurch et al., 2003b; Reinsel, 2002]. If there is less ozone  
19 depletion after 1997 than before, then ozone residuals after 1997 will show systematic positive  
20 values above the projected trend line (black dotted line). The 95% confidence limits for unbiased  
21 residuals appear as the black dotted traces in the right panels of Figure 3, where the limits  
22 increase with time due to unresolved fluctuations and uncertainty in the trend estimates.

23 If the autocorrelation of the error terms (i.e., the AR(1) term) is significant, two problems  
24 are expected in the ordinary least-squares fittings [e.g., see (8-56) and (8-60) of Johnston, 1984]:  
25 (1) The estimated trend ( $\omega$ ) is unbiased, but the standard deviation for  $\omega$  is underestimated and  
26 (2) the variance of  $U_t$  is also underestimated. The underestimation of the variance of  $U_t$  is not  
27 serious in this study because of the relatively large sampling size. The variances of mean level  
28 and trend estimates, however, should be corrected by a correction factor ( $cf$ ) =  $(1+r)/(1-r)$ , where  $r$

1 is an autocorrelation parameter. In addition, the cumulative residuals tend to have more  
2 dispersion in the presence of a positive autocorrelation. Therefore, the variance of the cumulative  
3 ozone residuals (predicted) is calculated as (see Appendix),

4

5  $\text{VAR}\{\text{CUSUM}\}$

6

7  $= \text{VAR}\{\text{CUSUM residuals}\} + n_2^2 * \text{VAR}\{\text{mean}\} + [\sum_2 (t - t_0)]^2 * \text{VAR}\{\text{trend}\}$

8

9  $\approx cf \cdot \sigma^2 \{n_2 + n_2^2 / n_1 + [\sum_2 (t - t_0)]^2 / \sum_1 (t - t_0)^2\}$ ,

10

11 where  $\sigma$  is a standard error of the residuals for 1979-1996,  $n_1$  is number of data before the  
12 turnaround point (1997.0),  $n_2$  is number of data after the turnaround point,  $t_0$  is the mean value of  
13  $t$  for 1979-1996 [see *Newchurch et al.*, 2003b]. The estimated autocorrelation parameters are  
14  $\sim 0.5$  for the MOD and  $\sim 0.4$  for the ground Dobson/Brewer data in this study, resulting in inflations  
15 of CUSUM uncertainties by  $\sim 70\%$  and  $\sim 50\%$  for the MOD and Dobson/Brewer data. However,  
16 the autocorrelation parameter for the SAGE ozone residuals above 18 km is 0.08 so that its trend  
17 and CUSUM uncertainty are much less affected by these autoregressive processes. We expect  
18 the AR(1) parameter to be larger in the total ozone column than in the stratospheric column  
19 above 18 km because of the altitude dependence of the ozone lifetime (decreasing with altitude).

20 The CUSUMs plotted in the right panels of Figure 3 for the corresponding measurements  
21 are by definition equal to zero at the start of 1997; the small fluctuations prior to 1997 represent  
22 deviations from an assumption of linear ozone depletion over time. The CUSUMs increase  
23 starting in 1997.0, rising significantly above the 95% confidence limits indicated by the black  
24 dotted envelope for years after 1997. For example, the CUSUM metric for the SAGE data is 76%  
25 at the end of data (2005.5), while a CUSUM of only 29% would be considered a  $2\sigma$  departure  
26 from the extended linear trend line if ozone loss over the 1979-1996 and 1997-2005 time periods  
27 had occurred at the same rate. The green parabolic traces show the expected CUSUM behavior  
28 for ozone levels held constant after 1997.0. The recovery signatures from both the

1 Dobson/Brewer networks and the MOD are highly significant, and reflect increases in total  
2 column ozone since 1997. The Dobson/Brewer and MOD CUSUM values are larger than the  
3 SAGE value, because the SAGE value is based on data acquired only above 18 km altitude. As  
4 we show below, the region between the tropopause and 18 km (TP-18 km) contributes  
5 significantly to trends in total column ozone. Recognizing the 2-sigma uncertainty envelopes  
6 shown on Figure 3, we find that taken together, these independent measurements provide  
7 compelling evidence that, outside of the polar regions, the decline in stratospheric ozone above  
8 18 km has slowed down significantly since the beginning of 1997 and the decline in total-column  
9 ozone has stopped entirely.

10 Figure 4 shows the SAGE/HALOE residual ozone time series between 18-25 km, for  
11 northern mid-latitudes (30-60°N, top panels), tropics (10°S-10°N, middle panels), and southern  
12 mid-latitudes (30-60°S, bottom panels). Because the HALOE ozone measurements are less  
13 sensitive to aerosol loadings than the SAGE measurements, this combined ozone data set  
14 consists of SAGE data before the Pinatubo eruption and HALOE data after the eruption. The  
15 regression of the EESC time series (top panel, Figure 2) onto these ozone time series results in  
16 the corresponding blue lines, representing an estimate of the ozone changes resulting from the  
17 cessation of increasing levels of stratospheric halogens that occurred in approximately 1997. The  
18 time series in the left panels and the CUSUM metrics in the right panels indicate close  
19 correspondence between the observed ozone changes (black traces) and this estimate of ozone  
20 changes due to the halogen loading (blue traces), for all three latitude regions.

21 Further confirmation that the changes in the ozone time series between 18-25 km are  
22 due to changes in halogen loading is provided by model estimates of the fraction of ozone loss  
23 due to halogens ( $\text{Loss}_{\text{MODEL}}$ ) over the time period 1979 to present. The regression of  $\text{Loss}_{\text{MODEL}}$   
24 onto the ozone time series is shown by the red lines on the left hand panels of Figure 4. The  
25 CUSUM of the regression is shown by the red lines on the right panels. For northern and  
26 southern mid-latitudes, the CUSUMs for the SAGE/HALOE ozone time series, for EESC, and for  
27  $\text{Loss}_{\text{MODEL}}$  provide an overall consistent picture of a change in linear trend near 1997, consistent

1 with the time of peak halogen loading. The slight sensitivity of these results to the year of change  
2 in linear trend (1997 is used here) is described below.

3 The only deviation from this consistent picture is apparent, but with fewer data points, for  
4 the tropical region from 2001 to present. Here, the CUSUM for residual ozone displays a lag of ~2  
5 years relative to the CUSUM for EESC (black and blue lines, middle right panel, Figure 4).  
6 Notably, the CUSUM for LOSS<sub>MODEL</sub> indicates that little change in the fractional loss of ozone due  
7 to halogens is expected (red curve) between 1979 and present. This behavior of LOSS<sub>MODEL</sub> is  
8 driven by a smaller relative contribution of halogens to total ozone loss compared to the other  
9 latitude regions, because in the tropical lower stratosphere, inorganic chlorine and bromine have  
10 yet to be fully released from their organic reservoirs. Loss of ozone by HO<sub>x</sub> radicals exerts the  
11 predominant chemical influence, and trends in ozone are sensitive to both dynamics and changes  
12 in H<sub>2</sub>O and CH<sub>4</sub>. As noted above, similar CUSUM curves for LOSS<sub>MODEL</sub> in the tropics are found  
13 using a tracer-tracer approach, rather than the more empirical approach (e.g., model constrained  
14 by measured HCl and NO<sub>x</sub>) used for the curve shown in Figure 4. The disagreement between  
15 CUSUMs for LOSS<sub>MODEL</sub> and EESC suggests a simple regression of residual ozone would not be  
16 appropriate for the tropical lower stratosphere. This appears to be borne out by the ozone time  
17 series, which does not display a statistically significant change in linear trend as is seen in the  
18 other regions. Furthermore, time series of zonal, monthly mean HALOE H<sub>2</sub>O and CH<sub>4</sub> in the  
19 tropics exhibit significant long-term variability, with a tendency towards lower values since ~2002.  
20 The HALOE H<sub>2</sub>O and CH<sub>4</sub> data suggest the tropical lower stratosphere has undergone significant  
21 recent change in the effect of both transport and thermodynamics on its overall composition.

22 To establish attribution of the improving ozone conditions, we examine measurements of  
23 ozone collected in various altitude regions. Three altitude regions are considered: tropopause to  
24 18 km, 18 to 25 km, and 25 km to the top of the atmosphere (TOA). Here, only data acquired in  
25 the northern hemisphere mid-latitudes are shown. Changes in ozone as a function of altitude in  
26 southern hemisphere mid-latitudes are challenging to define because SAGE I measurements  
27 below 18 km altitude are unreliable (in both hemispheres) and Lauder ozonesonde observations  
28 start in 1987. Figure 5 shows changes in ozone at 30-60°N for the three altitude regions noted

1 above, compared in this case to time series of EESC. The change in EESC is consistent with the  
2 measured ozone behavior in the 18-25 km layer. This correspondence strongly suggests that  
3 chemistry related to EESC changes, as opposed to dynamical changes, has been responsible for  
4 the ozone changes in this layer. The correspondence between EESC and the ozone time series  
5 and CUSUMs in Figure 4 support this conclusion.

6 Table 1 summarizes the estimated trends in ozone for the three altitude regions between  
7 30-60°N, as well as the total column, based on various data sets. The decline in total column  
8 ozone from 1979-1996 was  $-9.3 \pm 3.3$  (2 $\sigma$ ) DU/decade in the MOD record and  $-8.7 \pm 2.3$  (2 $\sigma$ ) in  
9 the Dobson/Brewer networks (Table 1). Ozonesondes yield a value of  $-2.1 \pm 1.6$  DU/decade for  
10 the change between the tropopause and 18 km. Trends of ozone in the 18-25 km layer are  $-3.9 \pm$   
11 0.9 based on only SAGE I/II,  $-4.7 \pm 1.3$  DU/decade based on the ozonesonde time series, and  
12  $-4.4 \pm 1.2$  DU/decade using the SAGE/HALOE record (all uncertainties throughout are 2 $\sigma$   
13 estimates). From 25 km to the TOA, SAGE indicates  $-4.3 \pm 1.0$  DU/decade was lost. Hence, we  
14 find that ~20% of the decline of total ozone from 1979-1996 was due to changes between the  
15 tropopause and 18 km, 38% of the drop occurred between altitudes of 18-25 km, and 42% of the  
16 change occurred above 25 km.

17 The altitude partitioning of the improvement in the stratospheric ozone layer starting in  
18 1997 is significantly different from the altitude partitioning of the decline (Table 1). The same data  
19 sets described above yield an improvement in total ozone column of  $16.3 \pm 6.6$  DU/decade from  
20 1997-2005 with respect to the declining trend line, with 49% of the improvement occurring  
21 between the tropopause and 18 km, 21% between altitudes of 18-25 km, and 30% due to ozone  
22 increases above 25 km.

23 The ozone changes in the tropopause to 18 km layer since 1997.0, as shown in Figure 5  
24 (bottom panel) and Table 1, are much larger than can be explained by known chemistry (i.e., the  
25 EESC fit accounts for only approximately 50 CDU of the calculated 389 CDU change, where CDU  
26 is cumulative DU). An analysis based on  $\text{Loss}_{\text{MODEL}}$ , using known photochemistry and established  
27 tracer relations, similarly fails to account for the observed features of the ozone time series (not  
28 shown). We should expect that some of the ozone change in the lower layer since 1997 results

1 from a change in the flux from the source layer above, because of the chemically induced ozone  
2 change in the 18-25 km layer, even if there is no change in the dynamics. Based on an ozone  
3 change of 249 CDU in the 18-25 km layer (average of 167 for SAGE, 309 for SAGE/HALOE and  
4 271 for ozonesondes, see Table 1), and because there is approximately twice as much ozone in  
5 this layer as in the tropopause to 18 km layer, a change of perhaps 124 CDU in the lower layer  
6 might be related to this change of the downward flux without any change in the dynamics.  
7 Combining this change with the EESC effect falls significantly short of accounting for the  
8 observed change of 389 CDU relative to the pre-1997 trend. Therefore, transport changes  
9 probably dominate the changes in ozone from 1997 to 2005, between the tropopause and 18 km,  
10 for the 30-60°N region.

11 Because of the slowly-varying changes in ozone depleting substances at the ground and  
12 the effect of mixing (which induces a spectrum to the mean age of air) [e.g., *Waugh et al.*, 2001;  
13 *Engel et al.*, 2002], the expected turnaround point for ozone cannot be precisely defined. Figure 6  
14 illustrates the sensitivity of the analysis to variations in the turnaround year, for residuals at 18-25  
15 km, 30-60°N, for SAGE ozone (left panels) and ozonesonde ozone (right panels) residuals. The  
16 late turnaround points in 1998 and 1999 result in more precise trend estimates and less  
17 uncertainty of the CUSUM envelopes, which are balanced by the smaller CUSUM values due to  
18 the smaller number of time steps for CUSUM calculations. Nonetheless, for turnaround in 1998 or  
19 1999, the CUSUMs for SAGE and ozonesonde residuals approach or exceed the 95%  
20 confidence intervals (black dotted lines) at the end of the time period. Assuming a turn around  
21 point of 1995.0 (top panels, Figure 6) is the only case where the CUSUM values fails to exceed  
22 the 95% confidence interval. In this case, the turn around point is close to the discontinuity  
23 caused by the data exclusion during the Pinatubo period. Figure 6, therefore, shows shifts of the  
24 turn around time by about one year forward from 1997.0, or two years after 1997.0, do not  
25 change the conclusions of this study.

26

27

28

1 **6. Relative roles of transport and chemistry**

2 Support for the inferred relative roles of chemistry and transport in producing the  
3 observed ozone changes since 1997.0 is provided by results shown in Figures 7 through 9. The  
4 residual column ozone at 18-25 km and TP-18 km in Figure 5 has significant periodicities of 3-5  
5 years. In order to show a clear long-term change in ozone, these ENSO-like signals are removed  
6 from the ozone time series [e.g., *Steinbrecht et al.*, 2005] only in Figures 7 and 8 in this study.  
7 Figure 7 displays results of the regression of EESC, temperature (T), tropopause height (TPH),  
8 and potential vorticity (PV) onto residual ozone values smoothed with a 13-month filter. The  
9 temperature, tropopause height, and potential vorticity are calculated at the same locations and  
10 times as the ozonesonde measurements, using NCEP reanalysis data. The cause of long term  
11 changes in temperature and tropopause height is difficult to assess, since each is sensitive to  
12 climate change as well as ozone depletion [e.g., *Santer et al.*, 2003]. Indeed, *Santer et al.* [2003]  
13 estimate, based on a climate model simulation, that declining ozone is the largest contributor to  
14 rising tropopause height over the 1979 to 1999 time period. However, rising levels of greenhouse  
15 gases are also expected to lead to significant increases in tropopause height. The changes in PV  
16 illustrated in Figure 7 are likely indicative of changes in Rossby wave breaking events that can  
17 clearly affect ozone time series in this region of the atmosphere [e.g., *Koch et al.*, 2002].  
18 However, PV can also change due to variations in static stability, and hence is not uncoupled  
19 from changes in tropopause height and temperature.

20 The analysis shown in Figure 7 indicates that variations of temperature, tropopause  
21 height and PV explain more of the ozone variance from 1979 to 2005 in the lower layer  
22 (tropopause to 18 km) than they explain in the 18 to 25 km region. The overall percentage of the  
23 ozone variance explained by EESC, relative to T, TPH, and PV is much larger for the 18-25 km  
24 region than the TP-18 km layer. However, as noted above, variations in T, TPH, and PV could be  
25 due to feedbacks related to ozone changes, or could be driven by changes in transport ultimately  
26 related to climate change.

27 To further explore the factors responsible for observed variations in ozone at different  
28 atmosphere levels, we examine the relation between these quantities over shorter time periods.

1 Figure 8, using a 3-month filter on ozone residuals, shows the close correspondence of ozone  
2 with T, TPH, and PV on time scales of a few months. We tested several proxies and found that  
3 except for ENSO, their influences on the long-term changes in ozone at 18-25 km are negligible,  
4 although the other proxies have some effects on the ozone below 18 km. The overall higher  
5 correlations of T, TPH, and PV with ozone residuals below 18 km, relative to the correlation with  
6 EESC, when residuals are examined for short term fluctuations provides further evidence that  
7 changes in ozone below 18 km are not driven by halogen chemistry. The weak correlations  
8 between these dynamical variables and ozone above 18 km, relative to the correlation of O<sub>3</sub> with  
9 EESC, suggests a weak contribution from changes in dynamics (or climate) to long-term changes  
10 in ozone above 18 km. Similarly, the weak correlation between EESC and ozone below 18 km  
11 shown in Figure 8 is indicative of small contribution of ClOx/BrOx chemistry to the long-term  
12 change in ozone below 18 km. Although temperature explains 48% and 38% of ozone variance at  
13 18-25 km in Figures 7 and 8, the linear decrease of temperature over the entire time period does  
14 not match the curved shape of the ozone residual at 18-25 km. The linear decrease of  
15 temperature over time, different in shape from the ozone time series, seems consistent with  
16 forcing from both changes in ozone and rising levels of greenhouse gases [e.g., Santer *et al.*,  
17 2003].

18 It has been suggested that the turnaround year of 1997 might pose a complication due to  
19 a number of cold Arctic winters that began in this time period [Weatherhead and Andersen, 2005].  
20 To investigate the influence of polar ozone loss on the extra-polar ozone time series, we examine  
21 the relation between residual ozone and the volume of air in the Arctic vortex exposed to polar  
22 stratospheric clouds (V<sub>PSC</sub>). It has been shown that V<sub>PSC</sub> is a good proxy for chemical loss of  
23 Arctic ozone [Rex *et al.*, 2004; Tilmes *et al.*, 2004; Chipperfield *et al.*, 2005]. Figure 9 compares  
24 the time series of residual ozone for various altitudes and latitudes, as indicated, to a time series  
25 for V<sub>PSC</sub> that is based on the same data points for each panel. The values of V<sub>PSC</sub> are calculated  
26 in the same manner as described by Rex *et al.* [2004]. The regressions of SAGE ozone residuals  
27 with V<sub>PSC</sub> appear as blue for regions showing negative correlations and are plotted as negative  
28 values to visually emphasize the correlation; red is used for regions showing positive correlations

1 between residual ozone and  $V_{PSC}$ . A negative correlation between  $V_{PSC}$  and residual ozone  
2 means that larger values of chemical loss of polar ozone are associated with decreases in the  
3 ozone abundance at mid-latitudes, as hypothesized by *Weatherhead and Andersen* [2005].  
4 Figure 9 shows the region of strong, negative correlations between  $V_{PSC}$  and SAGE ozone  
5 variations for 50-60°N, below ~16 km. These results suggest horizontal transport of chemically  
6 depleted ozone from the Arctic vortex might account for some of the observed negative trends in  
7 ozone for this region of the atmosphere. But, this influence appears to be confined mainly to  
8 altitudes below ~16 km, and latitudes poleward of 50°N. The regressions shown in Figure 9  
9 demonstrate that, for the majority of the extra-polar data considered here, the dominant changes  
10 in ozone are not driven by polar ozone chemical loss.

11 *Hadjinicolaou et al.* [2005] state “all of the observed upward trend [in total column ozone  
12 from MOD] from 1994 to 2003 are reproduced by the [SLIMCAT] model which is forced only by  
13 transport changes” [e.g., halogen levels are fixed at 1980’s levels]. This finding appears at first  
14 glance to be different from our results, which require both chemical and dynamical forcings to  
15 reproduce measured ozone residuals since 1997. Figure 1 and figure 2a in *Hadjinicolaou et al.*  
16 [2005] show that (1) the negative trend in total column ozone for 1979-1993 is mostly due to the  
17 increasing halogen loading for the same period and (2) the transport changes along with fixed  
18 halogen loading is mostly responsible for the rise in column ozone for 1994-2003. Their results,  
19 as shown in their figure 2a in particular, appear to us to require the existence of a substantial  
20 change in halogen loading, between 1980 and 1994, in order to explain the changes in column  
21 ozone over the entire time period. Note that their model with fixed halogen loading is predicting  
22 larger ozone values in 2003 than in 1980, which is contrary to observations shown here.

23 Positive changes in ozone since 1996 were also obtained from the MOD, SBUV(/2), and  
24 Dobson/Brewer total ozone data by *Reinsel et al.* [2005], who showed that the changes were  
25 significant both with and without the dynamical considerations. Their result indicates that the  
26 changes in total column ozone are attributable to chemistry as well as dynamics. Our study  
27 complements the analysis of *Reinsel et al.* [2005] by showing that the positive trend in ozone since

1 1996/1997 results both from the transport driven increases in ozone for the tropopause to 18 km  
2 layer and from predominantly chemical driven increases in ozone for altitudes above 18 km.

3 Finally, *Salawitch et al.* [2005] noted that bromine supplied to the stratosphere from  
4 biogenic bromine and tropospheric BrO could lead to larger amounts of ozone depletion, between  
5 the tropopause and ~18 km, compared to models that consider supply of bromine only from  
6  $\text{CH}_3\text{Br}$  and halons. The effect of biogenic bromine on ozone trends is most notable during time of  
7 elevated aerosol loading (figure 4 of *Salawitch et al.*). During periods of background loading, ClO  
8 levels are too small, below 18 km, for ozone loss by the  $\text{BrO}+\text{ClO}$  cycle to be efficient. We have  
9 conducted simulations using constant offsets to the  $\text{Br}_y$  relation based on the WMO Baseline Ab  
10 scenario for  $\text{CH}_3\text{Br}$  and halons (not shown), and the resulting values of  $\text{LOSS}_{\text{MODEL}}$  are unable to  
11 reproduce the large increases in ozone observed below 18 km since 1997. It is important to note  
12 that these simulations assumed constant offsets to  $\text{Br}_y$  (e.g., that the supply of bromine from short  
13 lived, biogenic bromocarbons and tropospheric BrO is constant over time). If the supply of  
14 biogenic bromine to the stratosphere had varied over time, with a strong decrease after 1997,  
15 then ozone levels would be expected to rise, due to the  $\text{BrO}+\text{HO}_2$  cycle (figure 5 of *Salawitch et*  
16 *al.*). However, values of  $\text{Br}_y$  inferred from balloon observations of BrO appear to exhibit a near  
17 constant offset relative to the bromine content of  $\text{CH}_3\text{Br}+\text{halons}$ , data that spans stratospheric  
18 entry dates of 1992 to 2002 [figure 1-8 of WMO, 2003; Dorf, 2005]. Therefore, we consider it  
19 unlikely that biogenic bromine could be responsible for the rise in ozone observed between 18 km  
20 and the tropopause since 1997.

21 We conclude that observed ozone changes in the 18-25 km layer since 1979 are  
22 consistent with chemical effects driven by increases in halogens. However, increases in ozone  
23 observed after 1997 between the tropopause and 18 km likely have had a significant transport  
24 component. About half of the observed increase in ozone since 1997 has occurred between the  
25 tropopause and 18 km.

26

27

28

1 **7. Conclusions**

2 Analyses of monthly stratospheric and total-column ozone values from three independent  
3 satellite instruments and two ground-based networks of sensors comprising combinations of the  
4 SAGE I/II, HALOE, merged TOMS/SBUV satellites, the Dobson/Brewer ground-based networks,  
5 and the global ozonesonde network indicate that the thickness of Earth's stratospheric ozone  
6 layer stopped declining after about 1997. Regression analyses of both EESC (effective equivalent  
7 stratospheric chlorine) and of more sophisticated photochemical calculations independently  
8 indicate that the temporal signature of the observed changes in ozone above 18 km altitude is  
9 consistent with the timing of peak stratospheric halogen abundances, which occurred mid-way  
10 through 1997. These results confirm the positive effect of the Montreal Protocol and its  
11 amendments on limiting the growth of stratospheric chlorine and bromine, and in protecting  
12 Earth's ozone layer.

13 Increases in stratospheric ozone at NH mid-latitudes since the mid-1990s are also  
14 observed for altitudes below 18 km. These increases appear to be driven principally by changes  
15 in atmospheric dynamics. The changes in ozone for this height region exhibit positive correlations  
16 with dynamical proxies such as potential vorticity and tropopause height, and do not bear the  
17 signature of expected long-term change due to stratospheric halogens. The rise in total column  
18 ozone since 1997, for NH mid-latitudes (30–60°N), appears to be caused by ~50% contribution  
19 from increases in ozone below 18 km altitude, and ~50% contribution from rising ozone above 18  
20 km. Hence, both chemical and dynamical forcings appear to be responsible for the observed rise  
21 in column ozone at NH mid-latitudes since 1997. Much work remains in order to understand  
22 whether the dynamically driven changes are due to natural variability or due to changes in  
23 atmospheric structure related to anthropogenic climate change. Furthermore, the recent  
24 observations of stratospheric ozone were obtained during a time of unusually low levels of  
25 stratospheric aerosol loading. Chemical reactions initiated by volcanic aerosol that penetrates the  
26 stratosphere, should a major eruption occur, will almost certainly lead to short periods of lower  
27 ozone due to ozone destruction by anthropogenic halogens in the presence of those aerosols.

1 We conclude by noting that our paper represents the complete data record from the  
2 remarkable SAGE and HALOE instruments. SAGE I commenced observations in 1979 and  
3 SAGE II ceased operating on August, 22 2005. HALOE ceased operating on December 14, 2005.  
4 The SAGE I/II and HALOE instruments documented ozone depletion due to rising CFCs, the start  
5 of the recovery of ozone (above 18 km) due to declining CFCs, and an unanticipated significant  
6 increase in ozone since 1997 (between the tropopause and 18 km) due most likely to changes in  
7 stratospheric transport. The data record provided by HALOE and SAGE played an important role  
8 in quantifying the effect of human activity on the ozone layer that led to the passage of the  
9 Montreal Protocol and its amendments that restricted the production of CFCs. The HALOE and  
10 SAGE II teams should be especially proud that these instruments recorded the beneficial effects  
11 of this landmark international legislation.

12

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19 study were obtained from the NASA/LaRC data center. Dobson/Brewer total ozone and  
20 ozonesonde ozone data were provided by the World Ozone and Ultraviolet Data Center  
21 (WOUDC) in Toronto, Canada and by the Swiss Meteorological Service. The merged  
22 TOMS/SBUV data were provided by NASA/GFSC. EESC data were provided by S.  
23 Montzka/NOAA/CMDL. We thank the three reviewers for their helpful comments and constructive  
24 criticism, and Markus Rex for sharing values of  $V_{PSC}$  used in this study. This work is dedicated to  
25 the memory of Professor Greg Reinsel.

1    **Figure Captions**

2

3    Figure 1. Comparison of modeled and measured HCl and NO<sub>x</sub>. Time series of zonal, monthly  
4    mean HCl and NO<sub>x</sub> measured by HALOE (black circles) at 20 and 25 km, for indicated  
5    latitude regions, compared to calculated values of HCl and NO<sub>x</sub> (red dots). Data and  
6    model results for HCl include sunrise and sunset points. Data and model results for NO<sub>x</sub>  
7    are shown only for sunset. The comparisons for sunrise (not shown) are comparable, but  
8    both measured and modeled NO<sub>x</sub> are lower than sunset values, due to the diurnal cycle  
9    of NO<sub>x</sub>. The simulations for the equatorial regions are constrained to measured HCl and  
10   model results for HCl during the UARS time period (Cl<sub>y</sub> and NO<sub>y</sub> are adjusted in the model); for earlier time  
11   periods, monthly mean values of Cl<sub>y</sub> and NO<sub>y</sub> normalized to 1993 are propagated  
12   backwards, using the known temporal changes in organic chlorine and N<sub>2</sub>O.

13

14   Figure 2. Time series of Equivalent Effective Stratospheric Chlorine, EESC, (upper) and fractional  
15   ozone loss rate due to halogens (lower). The fractional ozone loss rate (Loss<sub>MODEL</sub>)  
16   results from photochemical model calculations that are constrained by observations as  
17   described in the text. Fractional ozone loss rate is the ozone loss rate due to halogens  
18   divided by total ozone loss rate integrated from 18 to 25 km weighted by the ozone  
19   concentrations at each altitude in 7 latitude bands. The blue lines show the EESC series  
20   fitted to the fractional loss rates whose data are excluded during the Pinatubo period.

21

22   Figure 3. Time series of monthly average ozone residuals plus linear trend (left) and cumulative  
23   sum (CUSUM) of residuals (right) in % for the SAGE(black)/HALOE(red) stratospheric  
24   ozone columns above 18 km between 60°S-60°N (top panels), Dobson/Brewer total  
25   ozone columns 30°S-60°N (middle panels), and merged TOMS/SBUV (MOD) total ozone  
26   columns 60°S-60°N (bottom panels). The SAGE, HALOE, Dobson/Brewer, and merged  
27   TOMS/SBUV monthly residuals are all independently obtained by removing the seasonal,  
28   solar, and QBO terms from their respective ozone series. The trend line indicates the

1 ozone trend calculated from observations for 1979-1996 (solid line) and forecasted  
2 linearly afterward (dotted line). Linear trends and 95% confidence intervals for 1979-1996  
3 are listed. The ozone residuals during the Pinatubo period are shown in open circles, but  
4 they are excluded from the trend calculations. The last value in the cumulative residual  
5 time series represents the cumulative difference of all monthly residuals after 1997.0 with  
6 respect to the predicted trend line. The green line represents the hypothetical case where  
7 the ozone values remained at their 1997.0 value until 2005. The black dotted lines in the  
8 right panels indicate the 95% confidence envelopes of departure from natural variability  
9 and model uncertainty.

10

11 Figure 4. Time series of monthly ozone residuals plus linear trend (black trace in the left panels)  
12 and cumulative sum of residuals (black trace in the right panels) for the SAGE/HALOE  
13 data integrated from 18 to 25 km for 30-60°N (top panels), 10°S-10°N (middle panels),  
14 and 30-60°S (bottom panels). Tabulated trends correspond to 1979-1996 (black line in left  
15 panels) projected to 2005 (dotted black lines, left panels). The SAGE data are used for  
16 the period before the Pinatubo volcanic eruptions and HALOE data afterwards. The blue  
17 lines represent the ozone change estimated by the EESC fit (left) and its cumulative sum  
18 (right). The red lines show the ozone evolution expected from the photochemical  
19 calculations (left panels) and the cumulative sum of the ozone change estimated by the  
20 calculated fractional loss rate (right panels). The black dotted lines in the right panels  
21 indicate the 95% confidence envelopes of departure from natural variability and model  
22 uncertainty

23

24 Figure 5. Time series of monthly ozone residuals plus linear trends from SAGE (red traces in the  
25 left panels) and ozonesondes (black traces) at 30-60°N; cumulative sum in the right  
26 panels in DU. Top panels display SAGE I/II values above 25 km and the associated  
27 EESC fit. Middle panels display ozonesonde values from 11 stations (black), SAGE I/II  
28 (red) and EESC fit (blue) at 18-25 km. The ozone residuals during the El Chichon and

1 Pinatubo period are shown in open circles, but they are excluded from the trend  
2 calculations. Bottom panels display ozonesonde values (black) and SAGE II (red) with  
3 EESC fit to ozonesonde values (blue) between tropopause and 18 km.

4

5 Figure 6. CUSUM calculations for the SAGE (left panels) and ozonesonde (right panels) ozone  
6 residuals between 18-25 km, 30-60°N. The turnaround points are selected at 1995.0,  
7 1996.0, 1997.0, 1998.0, and 1999.0 (top to bottom panels, respectively).

8

9 Figure 7. Ozonesonde residuals plus trend (black traces) between tropopause-18 km (left panels)  
10 and 18-25 km (right panels) when additional ENSO-like signals (periodicities of 31-60  
11 months) are removed from the ozonesonde measurements between 30-60°N in Figure 5.  
12 Similarly, the respective residuals are calculated for temperature, tropopause height, and  
13 potential vorticity. These residuals are smoothed by a 13-month running mean to show  
14 their long-term changes. The ozone residuals are separately regressed against the EESC  
15 series (first panel) and temperature residuals (second panel), tropopause-height  
16 residuals (third panel), and potential-vorticity residuals (fourth panel). The estimated  
17 ozone responses are shown in blue lines for EESC, T, TPH, and PV, respectively. The  
18 percentage of the ozone variance explained individually by the exogenous variable is  
19 shown in the individual panels.

20

21 Figure 8. Same as in Figure 7, but smoothed by a 3-month (instead of 13-month) running mean to  
22 show the short-term fluctuations of ozone, EESC, temperature, tropopause height, and  
23 potential vorticity.

24

25 Figure 9. Time series of the volume of polar stratospheric air containing Polar Stratospheric  
26 Clouds (Vpsc) and SAGE ozone residuals at 50-60°N, 40-50°N, and 30-40°N from 10 to  
27 24 km. The ozone residuals for March and April are regressed onto the Vpsc values. The  
28 negative of the Vpsc series is plotted when the correlations are negative (blue line) in

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1 order to visually emphasize the correlations. The negative correlation coefficient is  
2 significant only below 18 km at 50-60°N.

3

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1   **Table 1.** Altitude distribution of decreasing trends, uncertainties, and fractional altitude  
 2   partitioning (1979-1996) from five different ozone records between 30-60°N and corresponding  
 3   average accumulation rates\*\*, uncertainties, and altitude partitioning (1997-2005).

4  
 5  
 6

Altitude Range	Instrument	Trend 1979-1996 [DU/decade]	Trend Uncertainty $2\sigma$	% of Total 1979-1996	CUSUM 1997-2005 CDU( $2\sigma$ )	Average Accumulation Rate [DU/decade]	Accumulation Rate Uncertainty $2\sigma$	% of Total 1997-2005
25 km-TOA	SAGE	-4.3	1.0	42	238 (141)*	4.9	2.9	30
18-25 km	Ozonesonde	-4.7	1.3	38	271 (206)	5.6	4.2	21
	SAGE	-3.9	0.9		167 (138)*	3.4	2.8	
	SAGE/HALOE	-4.4	1.2		309 (174)*	6.4	3.6	
	Average	-4.3	0.7			5.1		
TP-18 km	Ozonesonde	-2.1	1.6	20	389 (256)	8.0	5.3	49
$\Sigma$ layers	SAGE/ SAGE/sonde	-10.3	2.1		794 (323)	16.3	6.6	
Total Column	D/B	-8.7	2.3		845 (399)	17.4	8.2	
	MOD	-9.3	3.3					

7   \*mean ozone deviations assumed for missing data points.

8   \*\*The CUSUM value is the cumulative (consecutive) sum of the ozone residual deviations from  
 9   the projected trend line in the left panels of Figures 3 through 5. For a 1979-1996 trend estimate  
 10   of  $\omega_1$ , assuming a linear trend,  $\omega_2$ , after 1997.0, the ozone deviations from the 1979-1996 trend  
 11   line will follow the line,  $(\omega_2 - \omega_1) * t$ , with random fluctuations. Therefore,  $[CUSUM]_t = \text{Integral of}$   
 12    $(\omega_2 - \omega_1) * t = \frac{1}{2} * (\omega_2 - \omega_1) * t^2$ , where  $t$  is months. For example,  $[CUSUM]_t = 309$  CDU at  $t = 108$   
 13   months (9 years \* 12 months/year) in the upper panel of Figure 4. Then,  $309 = \frac{1}{2} * (\omega_2 - \omega_1) * t^2$   
 14   and  $(\omega_2 - \omega_1) = 6.4$  DU/decade. With  $\omega_1 = -4.4$  DU/decade in Figure 4,  $\omega_2 = 2.0$  DU/decade.  
 15   Therefore, the 1997-2005 average accumulation rate estimated by the CUSUM value is +2.0  
 16   DU/decade. This result is not a trend calculation, but rather an average accumulation rate with  
 17   the starting point (1997.0) fixed to the value of 1979-1996 trend line at 1997.0 with all data are  
 18   equally weighted. From this argument, however, it is clear that the change in trend at 1997.0 is  
 19   proportional to the CUSUM value.

20

1 **Appendix:**

2 When the error terms in the regression model are positively correlated, the ordinary least  
3 squares (OLS) estimates suffer the following two problems (e.g., *Johnston*, 1984).

4

5 1. The estimated regression coefficients are unbiased, but their error estimates could be  
6 underestimated.

7 2. The variance of ozone residuals is underestimated.

8

9 The second problem is not serious in this study because of large sampling size (~200). The  
10 variance of a cumulative sum of residuals, however, increases due to a positive autocorrelation of  
11 ozone residuals (see Section C).

12

## 13 A. AR(1) term in time series data

14 The typical trend model for ozone can be described as

15

$$16 [O_3]_t = c + \omega t + \alpha [S]_t + \beta [QBO]_t + \gamma [Solar]_t + U_t \quad (A1)$$

17

18 where  $c$  and  $\omega$  are constant and linear trend terms and  $[S]_t$ ,  $[QBO]_t$ , and  $[Solar]_t$  represent ozone  
19 variations due to season, QBO, and solar variations, respectively. Ozone trend plus error terms  
20 are now obtained by subtracting season, QBO, and solar variations from the original ozone time  
21 series, leading to the following expression:

22

$$23 [O_3]'_t = c + \omega t + U_t \quad (A2)$$

24

25 where  $U_t = \rho U_{t-1} + \varepsilon_t$  and  $\varepsilon_t$  is a white noise process (i.e., sequential errors are independent of  
26 each other). Even after removing ozone signals with phase (seasonal, QBO, and solar terms), the  
27 error term often shows a first-order autoregressive process, AR(1). The autocorrelated  
28 disturbance could be attributed mostly to missing explanatory variables, misspecification of the

1 form of regression, or characteristics of a data set. If the AR(1) parameter,  $\rho$ , is positive, the  
 2 estimates ( $c$  and  $\omega$ ) in Equation (A2) are unbiased but their standard errors are underestimated  
 3 [e.g., *Pindyck and Rubinfeld*, 1998].

4

5 In particular, at  $t-1$ , the above ozone series can be written as

6

7  $[O_3]_{t-1}' = c + \omega(t-1) + u_{t-1}$ . (A3)

8

9 Then,

10

11 using  $u_t = \rho u_{t-1} + \varepsilon_t$ ,

12

13  $[O_3]' - c - \omega t = \rho \{[O_3]_{t-1}' - c - \omega(t-1)\} + \varepsilon$ .

14

15 When introducing transformed variables,  $[O_3]^*_t$ ,  $c^*$ , and  $t^*$ , we obtain

16

17  $[O_3]^*_t = c^* + \omega^* t^* + \varepsilon$  (A4)

18

19 where

20  $[O_3]^*_t = [O_3]_t' - \rho [O_3]_{t-1}' = (1 - \rho B) [O_3]_t'$ ,

21

22  $c^* = c(1 - \rho) = (1 - \rho B)c$ ,

23

24  $t^* = t - \rho(t-1) = (1 - \rho B)t$ , and

25

26  $B$  is a backward shift operator, i.e.,  $B[O_3]_t' = [O_3]_{t-1}'$ .

27

1 In order to estimate the autocorrelation parameter  $\rho$ , we use the Hildreth-Lu procedure which  
 2 minimizes the error sum of squares in the transformed regression model (A4) [Neter et al., 1996].  
 3 The estimate of  $\rho$  is denoted here as  $r$ . The transformation reported by (A4) is the same as the  
 4 transformation used by the Yule-Walker procedure [Pankratz, 1983] and the results obtained here  
 5 are similar to the results obtained using that procedure.

6

7 B. Variance of CUSUM without an AR(1) term

8 If there is no AR(1) term in the regression model (A2), and if the ozone trend after the  
 9 turnaround point ( $T_o$ ) is the same as that before  $T_o$  (same-trend hypothesis), the variance of the  
 10 predicted ozone time series ( $[O_3]_t'$ ) after  $T_o$  is [Makridakis et al., 1983; Draper and Smith, 1998]:

11

12 Variance of predicted  $[O_3]_t'$

13

14  $= \text{VAR}\{\text{residuals}\} + \text{VAR}\{\text{mean estimate}\} + \text{VAR}\{\text{trend estimate}\}$

15

16  $= \sigma_u^2 \{1 + 1/n_1 + (t - \tau_1)^2 / \sum_1 (t - \tau_1)^2\}. \quad (B1)$

17

18 where

19  $\text{VAR}\{\text{residuals}\} = \sigma_u^2,$

20

21  $\text{VAR}\{\text{mean estimate}\} = \sigma_u^2 / n_1,$

22

23  $\text{VAR}\{\text{trend estimate}\} = \sigma_u^2 / \sum_1 (t - \tau_1)^2 = \sigma_u^2 / [(t_1 - \tau_1) + (t_2 - \tau_1) + \dots + (t_{n1} - \tau_1)]^2,$

24

25  $n_1 = \text{number of data prior to } T_o,$

26

27  $n_2 = \text{number of data from } T_o \text{ onward},$

28

1        $\tau_1$  = mean value of  $t$  prior to  $T_o$ , and

2

3        $\tau_2$  = mean values of  $t$  after  $T_o$ .

4

5       The first term in the right hand side of Equation (B1) arises from random noise and the second  
6       and third terms result from uncertainties in regression coefficients of mean and trend estimates.

7

8       The variance of CUSUM is a variance of the cumulative predicted- $[O_3]_t'$  such that

9

10      CUSUM variance of predicted  $[O_3]_t'$

11

$$12 = E[\{\sum_2 ([O_3]_t' - E[O_3]_t')\}^2]$$

13

$$14 = n_2 \cdot \text{VAR}\{\text{residuals}\} + n_2^2 \cdot \text{VAR}\{\text{mean estimate}\} + \sum_1 (t - \tau_1)^2 \cdot \text{VAR}\{\text{trend estimate}\}$$

15

$$16 = \sigma_u^2 \{n_2 + n_2^2 / n_1 + [\sum_2 (t - \tau_1)]^2 / \sum_1 (t - \tau_1)^2\}, \quad (B2)$$

17

18       where  $n_1$  is the number of data prior to  $T_o$  and  $E[x]$  is the expected value of  $x$ . The variance of  
19       CUSUM after  $T_o$  increases with  $t$ ,  $t^2$ , and  $t^4$  due to random fluctuations, uncertainty in mean level,  
20       and uncertainty in trend estimate, respectively [Newchurch et al., 2003b].

21

22      C. CUSUM variance with an AR(1) term

23       If the residuals are correlated in an AR(1) process, the regression model (A2) does not  
24       provide the correct uncertainty in the trend estimate. Instead, the regression model (A4)  
25       estimates an unbiased standard error of the ozone trend. Comparing models (A2) and (A4), we  
26       can see that the independent variable  $t^*$  converges to  $t$  when  $r \rightarrow 0$ . Since we are interested in  
27       ozone variations for actual time step ( $t$ ), (A4) divided by  $(1-rB)$  leads to,

28

$$1 \quad [O_3]' = c \left/ (1-r) \right. + \omega * t + \varepsilon \left/ (1-rB) \right. \quad (A4')$$

2

3         $\text{VAR}\{\text{predicted } [O_3]'\}$ 

4

5         $= \text{VAR}\{\text{residuals}\} + \text{VAR}\{\text{mean estimate}\} + \text{VAR}\{\text{trend estimate}\}$ 

6

$$7 \quad \approx \sigma_u^2 \{1 + 1/n_1 \cdot cf + (t - \tau_1)^2 / \sum_1 (t - \tau_1)^2 \cdot cf\} \quad (B1')$$

8

9        where

10

$$11 \quad \sigma_u^2 = \sigma_\varepsilon^2 / (1-r^2) \text{ from the relation } u_t = \rho u_{t-1} + \varepsilon_t,$$

12

$$13 \quad \text{VAR}\{\text{residuals}\} = \text{VAR}\{\varepsilon_t / (1-rB)\} = \text{VAR}\{(1 + rB + r^2B^2 + r^3B^3 + \dots) \varepsilon_t\} = \sigma_\varepsilon^2 / (1-r^2),$$

14

$$15 \quad \text{VAR}\{\text{mean estimate}\} = \sigma_\varepsilon^2 / (1-r)^2 / n_1 = \sigma_u^2 \cdot (1-r^2) / (1-r)^2 / n_1 = cf \cdot \sigma_u^2 / n_1,$$

16

$$17 \quad \text{VAR}\{\text{trend estimate}\} = \sigma_\varepsilon^2 / \sum(t^*)^2 = \sigma_\varepsilon^2 / [(1-r)^2 \sum(t)^2] = cf \cdot [\sigma_\varepsilon^2 / (1-r^2)] / \sum(t)^2,$$

18

$$19 \quad \text{and } cf = (1+r) / (1-r).$$

20

21        Due to the positive autocorrelations seen in most ozone time series, the ozone residuals  
 22        in the next step tend to follow the previous residual disturbances, resulting in more dispersion  
 23        from their expectation value. Indeed, a larger variance of CUSUM residuals is estimated if the  
 24        autocorrelation parameter  $r$  is positive.

25

26        At  $t = n_1 + 1$  (first data point after  $T_0$ ),

$$27 \quad E[u_t \cdot u_t]$$

$$\begin{aligned}
1 &= E[(\varepsilon_{n1+1} + r \varepsilon_{n1} + r^2 \varepsilon_{n1-1} + r^3 \varepsilon_{n1-2} + \dots) \cdot (\varepsilon_{n1+1} + r \varepsilon_{n1} + r^2 \varepsilon_{n1-1} + r^3 \varepsilon_{n1-2} + \dots)] \\
2 &= E[(\varepsilon_{n1+1}^2 + r^2 \varepsilon_{n1}^2 + r^4 \varepsilon_{n1-1}^2 + r^6 \varepsilon_{n1-2}^2 + \dots)] \\
3 &= \sigma_\varepsilon^2 + r^2 \sigma_\varepsilon^2 + r^4 \sigma_\varepsilon^2 + r^6 \sigma_\varepsilon^2 + \dots \\
4 &= 1 \cdot \sigma_\varepsilon^2 / (1-r^2)
\end{aligned}$$

5

6 At  $t = n_1 + 2$  (second data point after  $T_0$ ),

$$\begin{aligned}
7 &E[(u_t + u_{t-1}) \cdot (u_t + u_{t-1})] \\
8 &= E[\{(\varepsilon_{n1+2} + r \varepsilon_{n1+1} + r^2 \varepsilon_{n1} + r^3 \varepsilon_{n1-1} + \dots) + (\varepsilon_{n1+1} + r \varepsilon_{n1} + r^2 \varepsilon_{n1-1} + r^3 \varepsilon_{n1-2} + \dots)\} \cdot \{(\varepsilon_{n1+2} + r \\
9 &\varepsilon_{n1+1} + r^2 \varepsilon_{n1} + r^3 \varepsilon_{n1-1} + \dots) + (\varepsilon_{n1+1} + r \varepsilon_{n1} + r^2 \varepsilon_{n1-1} + r^3 \varepsilon_{n1-2} + \dots)\}] \\
10 &= E[(\varepsilon_{n1+2}^2 + (1+r)^2 \varepsilon_{n1+1}^2 + r^2 (1+r)^2 \varepsilon_{n1}^2 + r^4 (1+r)^2 \varepsilon_{n1-1}^2 + \dots)] \\
11 &= \sigma_\varepsilon^2 + (1+r)^2 / (1-r^2) \cdot \sigma_\varepsilon^2 \\
12 &= (2+2r) \cdot \sigma_\varepsilon^2 / (1-r^2)
\end{aligned}$$

13

14 At  $t = n_1 + 3$  (third data point after  $T_0$ ),

$$\begin{aligned}
15 &E[(u_t + u_{t-1} + u_{t-2}) \cdot (u_t + u_{t-1} + u_{t-2})] \\
16 &= E[\{(\varepsilon_{n1+3} + r \varepsilon_{n1+2} + r^2 \varepsilon_{n1+1} + r^3 \varepsilon_{n1} + \dots) + (\varepsilon_{n1+2} + r \varepsilon_{n1+1} + r^2 \varepsilon_{n1} + r^3 \varepsilon_{n1-1} + \dots) + (\varepsilon_{n1+1} + r \\
17 &\varepsilon_{n1} + r^2 \varepsilon_{n1-1} + r^3 \varepsilon_{n1-2} + \dots)\} \cdot \{(\varepsilon_{n1+3} + r \varepsilon_{n1+2} + r^2 \varepsilon_{n1+1} + r^3 \varepsilon_{n1} + \dots) + (\varepsilon_{n1+2} + r \varepsilon_{n1+1} + r^2 \varepsilon_{n1} + r^3 \varepsilon_{n1-1} \\
18 &+ \dots) + (\varepsilon_{n1+1} + r \varepsilon_{n1} + r^2 \varepsilon_{n1-1} + r^3 \varepsilon_{n1-2} + \dots)\}] \\
19 &= E[(\varepsilon_{n1+3}^2 + (1+r)^2 \varepsilon_{n1+2}^2 + (1+r+r^2)^2 \varepsilon_{n1+1}^2 + r^2 (1+r+r^2)^2 \varepsilon_{n1}^2 + r^4 (1+r+r^2)^2 \varepsilon_{n1-1}^2 + \dots)] \\
20 &= \sigma_\varepsilon^2 + (1+r)^2 \cdot \sigma_\varepsilon^2 + (1+r+r^2)^2 / (1-r^2) \cdot \sigma_\varepsilon^2 \\
21 &= (3+4r+2r^2) \cdot \sigma_\varepsilon^2 / (1-r^2)
\end{aligned}$$

22

23 At  $t = n_1 + 4$  (fourth data point after  $T_0$ ),

$$\begin{aligned}
24 &E[(u_t + u_{t-1} + u_{t-2} + u_{t-3}) \cdot (u_t + u_{t-1} + u_{t-2} + u_{t-3})] \\
25 &= E[\{(\varepsilon_{n1+4} + r \varepsilon_{n1+3} + r^2 \varepsilon_{n1+2} + r^3 \varepsilon_{n1+1} + \dots) + (\varepsilon_{n1+3} + r \varepsilon_{n1+2} + r^2 \varepsilon_{n1+1} + r^3 \varepsilon_{n1} + \dots) + (\varepsilon_{n1+2} + \\
26 &r \varepsilon_{n1+1} + r^2 \varepsilon_{n1} + r^3 \varepsilon_{n1-1} + \dots) + (\varepsilon_{n1+1} + r \varepsilon_{n1} + r^2 \varepsilon_{n1-1} + r^3 \varepsilon_{n1-2} + \dots)\} \cdot \{(\varepsilon_{n1+4} + r \varepsilon_{n1+3} + r^2 \varepsilon_{n1+2} + r^3 \\
27 &\varepsilon_{n1+1} + \dots) + (\varepsilon_{n1+3} + r \varepsilon_{n1+2} + r^2 \varepsilon_{n1+1} + r^3 \varepsilon_{n1} + \dots) + (\varepsilon_{n1+2} + r \varepsilon_{n1+1} + r^2 \varepsilon_{n1} + r^3 \varepsilon_{n1-1} + \dots) + (\varepsilon_{n1+1} + r \\
28 &\varepsilon_{n1} + r^2 \varepsilon_{n1-1} + r^3 \varepsilon_{n1-2} + \dots)\}]
\end{aligned}$$

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$$1 \quad = E[(\varepsilon_{n1+4}^2 + (1+r)^2 \varepsilon_{n1+3}^2 + (1+r+r^2)^2 \varepsilon_{n1+2}^2 + (1+r+r^2+r^3)^2 \varepsilon_{n1+1}^2 + r^2 (1+r+r^2+r^3)^2 \varepsilon_{n1}^2 + r^4$$

$$2 \quad (1+r+r^2+r^3)^2 \varepsilon_{n1-1}^2 + \dots)]$$

$$3 \quad = \sigma_\varepsilon^2 + (1+r)^2 \cdot \sigma_\varepsilon^2 + (1+r+r^2)^2 \cdot \sigma_\varepsilon^2 + (1+r+r^2+r^3)^2 / (1-r^2) \cdot \sigma_\varepsilon^2$$

$$4 \quad = (4+6r+4r^2+2r^3) \cdot \sigma_\varepsilon^2 / (1-r^2)$$

5 .

6 .

7 .

8 At  $t = n_1 + n_2$  (last data point),

$$9 \quad E[(u_t + u_{t-1} + u_{t-2} + u_{t-3} + \dots) \cdot (u_t + u_{t-1} + u_{t-2} + u_{t-3} + \dots)]$$

$$10 \quad = E[(\{\varepsilon_{n1+n2} + r \varepsilon_{n1+n2-1} + r^2 \varepsilon_{n1+n2-2} + r^3 \varepsilon_{n1+n2-3} + \dots\} + (\varepsilon_{n1+n2-1} + r \varepsilon_{n1+n2-2} + r^2 \varepsilon_{n1+n2-3} + r^3$$

$$11 \quad \varepsilon_{n1+n2-4} + \dots) + \dots] \cdot (\{\varepsilon_{n1+n2} + r \varepsilon_{n1+n2-1} + r^2 \varepsilon_{n1+n2-2} + r^3 \varepsilon_{n1+n2-3} + \dots\} + (\varepsilon_{n1+n2-1} + r \varepsilon_{n1+n2-2} + r^2 \varepsilon_{n1+n2-3} +$$

$$12 \quad r^3 \varepsilon_{n1+n2-4} + \dots) + \dots)]$$

$$13 \quad = E[(\varepsilon_{n1+n2}^2 + (1+r)^2 \varepsilon_{n1+n2-1}^2 + (1+r+r^2)^2 \varepsilon_{n1+n2-2}^2 + \dots + (1+r+r^2+\dots+r^{n2})^2 \varepsilon_{n1+n2-1}^2 + r^2$$

$$14 \quad (1+r+r^2+\dots+r^{n2})^2 \varepsilon_{n1}^2 + r^4 (1+r+r^2+\dots+r^{n2})^2 \varepsilon_{n1-1}^2 + \dots)]$$

$$15 \quad = \sigma_\varepsilon^2 + (1+r)^2 \cdot \sigma_\varepsilon^2 + (1+r+r^2)^2 \cdot \sigma_\varepsilon^2 + (1+r+r^2+r^3)^2 \cdot \sigma_\varepsilon^2 + \dots + (1+r+r^2+\dots+r^{n2})^2 / (1-r^2) \cdot \sigma_\varepsilon^2$$

$$16 \quad = \{n_2 + 2(n_2-1)r + 2(n_2-2)r^2 + 2(n_2-3)r^3 + \dots + 2(1)r^{n2-1}\} \cdot \sigma_\varepsilon^2 / (1-r^2)$$

$$17 \quad \approx \{n_2 + 2n_2r / (1-r)\} \cdot \sigma_\varepsilon^2 / (1-r^2)$$

$$18 \quad = n_2 \cdot (1+r) / (1-r) \cdot \sigma_\varepsilon^2 / (1-r^2)$$

$$19 \quad = \sigma_\varepsilon^2 / (1-r^2) \cdot n_2 \cdot cf$$

20

21 Because of the sufficiently large number of  $n_2$  in this study (108 months from 1997 to 2005), the

22 variance of the CUSUM residuals approaches  $\sigma_\varepsilon^2 / (1-r^2) \cdot n_2 \cdot cf$ . Therefore, the variance of the

23 CUSUM is calculated as

24

$$25 \quad \text{VAR}\{\text{cumulative predicted-}[\text{O}_3]_t'\}$$

26

$$27 \quad = \text{VAR}\{\text{CUSUM residuals}\} + n_2^2 \cdot \text{VAR}\{\text{mean estimate}\} + [\sum_2 (t - \tau_1)]^2 \cdot \text{VAR}\{\text{trend}\}$$

28 estimate}

1

2 
$$\approx cf \cdot \sigma_u^2 \{n_2 + n_2^2 / n_1 + [\Sigma_2(t - \tau_1)]^2 / \Sigma_1(t - \tau_1)^2\} \quad (B2')$$

3

4 In the above derivations, we neglect uncertainty in an estimated  $r$ . Compared to the CUSUM  
5 variances without an AR(1) term, (B2') now shows that the variances increase by a correction  
6 factor,  $(1+r)/(1-r)$ .

7

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